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PB80-149552

Technical Assistance Document for the Calibration of Ambient Ozone Monitors

(U.S.) Environmental Monitoring and Support Lab,
Research Triangle Park, NC

Sep 79

PB80-149552

United States
Environmental Protection
Agency

Environmental Monitoring and Support
Laboratory
Research Triangle Park NC 27711

EPA-600/4-79-057
September 1979

Research and Development

EPA

Technical Assistance Document for the Calibration of Ambient Ozone Monitors

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1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA 600/4-79-057		PB 80 149552

4. TITLE AND SUBTITLE TECHNICAL ASSISTANCE DOCUMENT FOR THE CALIBRATION OF AMBIENT OZONE MONITORS	5. REPORT DATE September 1979 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Richard J. Paur, ESRL/RTP Frank F. McElroy, EMSL/RTP	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Quality Assurance Division Environmental Monitoring Systems Laboratory U.S. Environmental Protection Agency Research Triangle Park, NC 27711	10. PROGRAM ELEMENT NO. 1AD800 11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Monitoring Systems Laboratory Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, NC 27711	13. TYPE OF REPORT AND PERIOD COVERED Final 14. SPONSORING AGENCY CODE EPA 600/08

15. SUPPLEMENTARY NOTES

Technical Assistance Document

16. ABSTRACT

In February, 1979, EPA revised certain parts of the ambient air pollution monitoring regulations (40 CFR Part 50, Appendix D) to specify a new procedure for calibration of ambient ozone analyzers. The new procedure is based on ultraviolet (UV) absorption photometry, and specifies in detail the UV photometer, other apparatus, and the procedure necessary for establishing quasi-primary ozone concentration standards derived from the known absorption coefficient of ozone at 254 nm.

This Technical Assistance Document is intended to provide information and assistance to State monitoring agencies and other organizations which must use the new procedure to calibrate ambient ozone analyzers. The first section of the document is a discussion of absorption photometry, with emphasis on the transmittance measurement and measurement errors. Section 2 provides step-by-step explanatory information and advice keyed to each paragraph of the procedure. Section 3 discusses UV photometers specifically, their design and operational characteristics, and several commercially available models.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air pollution Measurement Calibration Air pollution monitoring	Ozone analyzer Ozone standards UV photometry Technical assistance document	68A 43F

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	
	20. SECURITY CLASS (This page)	22. PRICE
	UNCLASSIFIED	

EPA Form 2220-1 (9-73)

TECHNICAL ASSISTANCE DOCUMENT FOR THE CALIBRATION OF AMBIENT OZONE MONITORS

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FOREWORD

Measurement and monitoring research efforts are designed to anticipate potential environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina has responsibility for: assessment of environmental monitoring technology and systems; implementation of agency-wide quality assurance programs for air pollution measurement systems; and supplying technical support to other groups in the Agency, including the Office of Air, Noise and Radiation, the Office of Toxic Substances, and the Office of Enforcement.

The ultraviolet photometric procedures and guidance described in this Technical Assistance Document represent new monitoring technology which is now available to assist monitoring agencies in accurately calibrating ambient ozone analyzers and in assuring the continual quality of atmospheric ozone measurements.

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PREFACE

Analyzers designated as reference methods for the measurement of ozone in ambient air are based on the chemiluminescent reaction of ozone with ethylene. Such ozone analyzers are calibrated by having the instrument sample a calibration atmosphere and adjusting the instrument so that its output indicates the concentration of ozone present in the calibration atmosphere. Calibration atmospheres are obtained by means of the calibration procedure prescribed in 40 CFR Part 50, Appendix D.

The U.S. Environmental Protection Agency has replaced the original calibration procedure, promulgated in 1971, with a new procedure based on ultraviolet absorption photometry (U.S. Environmental Protection Agency 1979). The purpose of this document is to provide the user community with information to aid in successful adoption of the new calibration procedure.

This document is organized into three major sections. The first section is a discussion of absorption photometry, with primary emphasis on measurement of the transmittance of gaseous samples. Section 2 provides a step-by-step explanation of the new photometric ozone calibration procedure. Section 3 discusses the construction of photometers and provides the reader with some of the considerations to be addressed when designing a photometer. This last section also describes commercially available photometric systems.

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ACKNOWLEDGMENTS

The authors gratefully acknowledge the invaluable assistance of Michael E. Beard, John C. Puzak, Kenneth A. Rehme, and many others who contributed information and suggestions, reviewed the manuscript, or otherwise assisted in the preparation of this document.

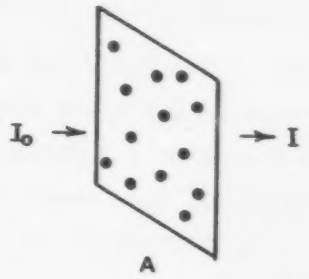
SECTION 1

THEORY OF PHOTOMETRIC MEASUREMENTS

A brief review of the theory of photometric measurements should help the reader more fully appreciate the advantages and shortcomings of photometry.

PHYSICAL BASIS OF THE PHOTOMETRY EQUATIONS

Consider the transmission of light through a plane of area A which contains some number, n, of absorbing molecules. If radiation of intensity I_o



is perpendicularly incident on the plane, and light of intensity I emerges from the plane, the transmittance, T, of the plane is defined as

$$T \equiv \frac{I}{I_o}$$

The transmittance is equal to

1 - fraction of light not transmitted

1. THEORY/Physical Basis of the Photometry Equations

or $$1 - \frac{\text{area blocked by absorbing molecules}}{\text{area of the plane, A}}$$

The area blocked by the absorbing molecules is equal to the product of the area blocked by a single molecule times the number of molecules, and the equation can be written as

$$T = 1 - \frac{n \times \sigma}{A} \qquad \text{(Eq. 1)}$$

where σ is the effective absorption cross-sectional area of the absorbing species. The units of σ are cm^2/molecule; σ is a measure of the molecule's capacity to block light by absorbing it. It is often useful to consider σ to be a measure of the effective size of the molecule.

The value of the effective absorption cross-sectional area depends on:

1. The nature of the absorbing species; i.e., some species absorb light of a given wavelength (λ) while others do not.
2. The wavelength of the light; i.e., the absorption of light by a molecule is different at different wavelengths. This property is what gives a species its characteristic spectrum. In terms of a simple model, this means that the effective size of a molecule is a function of the wavelength of light used to observe it.
3. The temperature and pressure of the gas when observing spectroscopic transitions in which both the upper and lower states are bound, i.e., under conditions where the observed spectrum is a sharp line. Since the ozone spectrum in the 250 nm wavelength region is primarily a broad continuum, the absorption cross section is only slightly dependent on temperature and pressure (Griggs 1968). To within the accuracy required for measuring ozone photometrically at 254 nm, one can assume that σ is a constant over ordinary temperatures and pressures.

1. THEORY/Physical Basis of the Photometry Equations

Since the sample cell in a photometer is of some finite length instead of being a plane, Equation 1 can be rewritten as

$$T = 1 - \frac{n \times \sigma \times \ell}{A \times \ell} = 1 - \left(\frac{n}{V} \times \sigma \times \ell \right) \qquad \text{(Eq. 2)}$$

where ℓ is the length of the sample cell and V is the volume of the sample cell. The term n/V is a concentration in units of number density. The fact that the transmittance of a sample depends on the number density of the absorbing species is convenient because it allows one to correct photometric measurements for the temperature and pressure of the sample by simple gas law calculations.

Most chemists, air pollution technicians, and other workers making photometric measurements prefer to use concentration units of atmospheres* and absorption coefficients in units of $atm^{-1}cm^{-1}$ instead of molecules/cm^3 and cm^2/molecule, respectively. The gas law can be written

$$P\ (atm) = \frac{n\ (molecules)}{V\ (cm^3)} \times R\ \frac{(cm^3 atm)}{(molecules\ K)} \times T\ (K)$$

Therefore, Equation 2 can be changed to atmospheres by multiplying the number density term by RT and dividing the absorption cross section by the same factor. Letting

$$\frac{n\ (molecules)}{V\ (cm^3)} = \frac{P\ (atm)}{RT\ \frac{(cm^3 atm)}{(molecules)}}$$

and

$$\alpha\ (atm^{-1}cm^{-1}) = \frac{\sigma\ (cm^2/molecule)}{RT\ \frac{(cm^3 atm)}{(molecule)}}$$

*A concentration of 1 atm equals the concentration of a gas at 1 atmosphere of pressure and standard temperature of 0° C.

Equation 2 becomes

$$T = 1 - \alpha P \ell = \frac{I}{I_o} \qquad \text{(Eq. 3)}$$

This very useful form of the photometry equation will be utilized later. First, consider the conditions for which the equation was derived. A basic assumption in the derivation is that the fraction of the light beam blocked by the absorbing molecules equals

$$\frac{n \times \sigma}{A}$$

or that the cross-sectional area of the beam that is blocked is n x σ. This assumption is valid only if the number of absorbing molecules in the sample is so small that one molecule never "shades" another. As soon as one molecule begins to shade another, the cross-sectional area of the beam that is blocked by these two molecules is less than 2σ.

To extend Equation 3 to the concentration and/or cell length range where significant shading of one molecule by others occurs (i.e., the concentration range where one normally applies photometry), the length of the absorption volume is divided into small segments, $d\ell$, such that there is no shading within any small segment. The cumulative result is obtained by "adding" the intermediate result from each segment by mathematical integration. Thus, Equation 3 is rewritten as

$$I_o - I = I_o \alpha P \ell$$

In integral form, this becomes

$$\int \frac{dI}{I} = -\int \alpha P \, d\ell$$

or

$$\ln I = - \alpha P \ell + C$$

When $P = 0$, $I = I_o$; therefore $C = \ln I_o$. The equation then becomes

$$\ln \frac{I}{I_o} = - \alpha P \ell$$

or

$$T = \frac{I}{I_o} = e^{-\alpha P \ell} = 10^{-\alpha P \ell / 2.30259} = 10^{-\alpha' P \ell} \qquad \text{(Eq. 4)}$$

Equation 4 is the form of the photometry equation that is probably most familiar to the majority of workers. It is valid over wide concentration and cell length ranges. Equation 4 is usually designated as the Bouguer-Lambert-Beer law or the Lambert-Beer law. The absorption coefficient, α', is called the absorptivity and is usually written simply as α when working in base 10. The concentration is normally designated by the letter c, and in most common usage Equation 4 is written as

$$T = \frac{I}{I_o} = 10^{-\alpha c \ell} = e^{-2.30259 \alpha c \ell} \qquad \text{(Eq. 5)}$$

Note that Equation 5 contains five terms (I, I_o, α, c, and ℓ), all of which can be measured. Furthermore, it is the ratio of I to I_o which is important rather than the absolute values of those quantities.

Frequently the Lambert-Beer law is written in logarithm form, with the term absorbance, A, often used to represent -log T:

$$A \equiv -\log T = \alpha c \ell$$

When the absorbance (i.e., the difference between I and I_o) is very small (as is typically the case when measuring the absorbance of sub-ppm levels of ozone), the Lambert-Beer law can be approximated in a linear form.

1. THEORY/Physical Basis of the Photometry Equations

$$T = \frac{I}{I_o} = e^{-\alpha c \ell} \approx 1 - \alpha c \ell \qquad \text{(Eq. 6)}$$

$$(e^{-x} = 1 - x \text{ for } x << 1)$$

Note that this approximation is identical to Equation 3. The error introduced by this approximation is not significant for ozone concentrations smaller than ~1 ppm (assuming a pathlength of <1 m), as will be shown below.

SOURCES OF ERROR INVOLVED IN THE PRINCIPLE

The relative error in the concentration measurement is related to the relative error in the determinations of α, ℓ, and T by the equations

$$\frac{dc}{c} = - \frac{d\alpha}{\alpha} \text{ (assuming no error in } \ell \text{ or T)}$$

$$\frac{dc}{c} = - \frac{d\ell}{\ell} \text{ (assuming no error in } \alpha \text{ or T)}$$

$$\frac{dc}{c} = - \frac{dT}{T \ln T} \text{ (assuming no error in } \alpha \text{ or } \ell)$$

The total error is the sum of these contributions.

The length of the optical path through the sample can normally be measured in a straightforward manner. The relative error associated with ℓ should not exceed ±0.5%, and in most systems is probably no larger than 0.1%. The absorptivity of a given species is measured in separate experiments and is normally available in the literature. The absorptivity of ozone at 254 nm has been determined by several workers (Table 1-1). A review of the literature (Hampson 1973) has placed the value of α at 308 ± 4 $atm^{-1}cm^{-1}$ (to base e) or 134 ± 2 $atm^{-1}cm^{-1}$ (to base 10). The absorptivity is normally given at standard temperature and pressure (STP) (273 K and 760 torr); the value used in a given experiment must be corrected via gas law calculations to reflect the pressure and temperature of the sample being measured.

1. THEORY/Sources of Error Involved in the Principle

TABLE 1-1. OZONE ABSORPTIVITY

Investigator(s), Year	α ($atm^{-1}cm^{-1}$, base e)	Method
Inn and Tanaka 1953	306.2	Manometry
Griggs 1968	303.9	Manometry
Becker et al. 1974	310.8	Manometry
Hearn 1961	308.5	Decomposition stoichiometry
DeMore and Raper 1964	310.8	Decomposition stoichiometry
Clyne and Coxon 1968	313.2 (250 nm)	GPT

To make the transmittance measurement, the absorption cell is filled with a reference gas (zero air in the case of ozone), and the intensity of the light passing through the cell is recorded as I_o. The absorption cell is then filled with the sample, and the intensity of the light passing through the cell is recorded as I.

The error in the measurement of T is multiplied by the term 1/lnT. For a typical value of T of 0.99385 (0.2 ppm O_3; 100 cm path), this term is ~160. Thus the transmittance measurement must be accurate to 1 part in 16000 to obtain a concentration accurate to 1% under the given conditions. Depending on one's choice of hardware, the transmittance measurement can be made with an accuracy of 1 part in 10^5 or better.

SECTION 2

STEP-BY-STEP DISCUSSION OF THE ULTRAVIOLET PHOTOMETRIC CALIBRATION PROCEDURE

This chapter provides explanation, augmentation, and general guidance to assist the user in carrying out each step of the ultraviolet (UV) photometric calibration procedure. The identification numbers and headings correspond directly to those used in the procedure. The complete procedure is presented as Appendix A and should be referred to as appropriate while reading the following step-by-step discussion.

1. Principle. This section discusses the principle of UV absorption photometry upon which the calibration procedure is based. Note that the concentration unit in Equations 1 and 2a in Appendix A is "atmospheres." A concentration of 1 atmosphere is equivalent to the concentration of a gas at a pressure of 1 atmosphere and a temperature of 0° C. The unit is used here to be consistent with the corresponding unit for the absorption coefficient α, which is given in the literature in $atm^{-1}cm^{-1}$. In Equation 2b in Appendix A, note that multiplication by 10^6 transforms the unit from atmospheres to parts per million, the familiar dimensionless volume ratio concentration unit. The minus sign in Equations 2a and 2b in Appendix A is needed because I should always be less than I_o; therefore, I/I_o is less than 1 and the natural logarithm (ln) of I/I_o is negative.

2. Applicability. Basically, the procedure is designed for calibration of ambient O_3 monitors; in many ways, it resembles calibration procedures for SO_2, NO_2, or CO ambient monitors. There is one very important difference, however. Calibration procedures for SO_2, NO_2, and CO analyzers call for externally obtained concentration standards traceable to primary standards

(Standard Reference Materials) obtained from the National Bureau of Standards (NBS). No Standard Reference Material is available for O_3. Therefore, any O_3 calibration procedure must include a built-in means for obtaining O_3 concentration standards based on some non-O_3 standard. In the photometric calibration procedure, O_3 concentration standards are related to the absorption coefficient of O_3 at 254 nm, as discussed in Section 1. Thus the procedure is more than a calibration procedure — it is also a means for obtaining O_3 concentration standards. Moreover, because the photometric procedure is prescribed by EPA regulations (U.S. Environmental Protection Agency 1979), and because no more authoritative O_3 standards are available from NBS, the O_3 concentration standards obtained by this photometric procedure are tantamount to primary ozone standards.

Because the photometric procedure is so important in obtaining primary O_3 standards, the procedure itself is sometimes called a "UV standard" for O_3 concentrations. This is simply an idiomatic expression referring, of course, to the O_3 concentrations obtained by means of the photometric procedure.

Note that the calibration procedure may also be used to certify transfer standards, which can then be used to calibrate ambient O_3 monitors. Such transfer standards must meet certain requirements and must be used properly. Requirements for transfer standards and guidance in their use are given in a companion EPA Technical Assistance Document (McElroy 1979).

3. Apparatus. The UV calibration system must include an O_3 generator, an output port or manifold, a photometer, a source of zero air, and whatever other components are necessary to provide a stable O_3 concentration output. The common configuration shown in Figure 1 of Appendix A is the basis for the procedural description. Another similar configuration uses a slightly pressurized system to eliminate the need for the pump to draw sample flow through the photometer. These configurations have been used successfully and are

probably near-optimum. Other variations are not precluded but would require critical evaluation for possible adverse effects.

Variations in the configuration may be inevitable to accommodate different photometers, various types of analyzers or transfer standards, and alternate O_3 generators. In particular, transfer standards containing their own sources of O_3 may require modification of the configuration; see McElroy (1979) for guidance. Any variations must be evaluated carefully to insure no adverse effects to the accuracy of the system.

O_3 is highly reactive and subject to losses upon contact with surfaces. All components between the O_3 generator and the absorption cell should be made of glass, Teflon, or other nonreactive material. Lines and interconnections should be kept as short as possible, and all surfaces must be very clean. Also, systems may need to be "conditioned" (operated with O_3 flowing at maximum concentration) for 10 to 30 minutes initially and sometimes before each use to minimize losses of O_3.

It is advantageous that both the output manifold and the photometer cell be at atmospheric pressure. Hence, components, lines, connections, and vents located between those items should be large enough to avoid any significant pressure drop at the highest flow used. Note the vent located between the zero air supply and the two-way valve. This vent is used to insure identical pressure conditions in the photometer cell during both modes of the valve.

3.1 UV photometer. The photometer is discussed in detail in Section 3.

3.2 Air flow controllers. The photometric measurement of absorption is not directly related to flow rate but may be indirectly related due to thermal or other effects. Thus, equal flow through the photometer cell during the two modes of the two-way valve may be important. The output of the O_3 generator is affected by flow changes, so good flow regulation for F_O is necessary.

Adequate flow regulation can be obtained by means of a pressure regulator and a needle valve or capillary, but more sophisticated flow control devices would certainly be acceptable.

3.3 Ozone generator. The O_3 generator must be very stable over short periods to facilitate the sequential photometric measurement of I_o and I, and to allow for stabilization of the analyzer or transfer standard connected to the output manifold. Conventional UV-photolytic type generators are adequate but should have line voltage and temperature regulation if possible. Mechanically or electrically adjustable generators are most convenient.

Where the O_3 generator is part of a transfer standard, special consideration is needed; see McElroy (1979).

3.4 Output manifold. The output manifold serves the important function of providing an interface between the calibration system and other devices or systems that utilize the output O_3 concentrations. The manifold must have one or more ports for connection of such external devices or systems, and it must be designed so that all ports of a multiport manifold provide identical concentrations. A very important part of the output manifold is the vent, which exhausts excess gas flow from the system and insures that the manifold outlet port or ports are kept at atmospheric pressure for all flowrates. The vent must thus be large enough to avoid any appreciable pressure drop and must be located sufficiently downstream of the output port to insure that no ambient air enters the manifold due to eddy currents, back diffusion, etc. The manifold may range from an elaborate, specially fabricated multiport fixture to a simple ordinary "T" fitting where one of the legs is used as a vent. The manifold must be made of glass, Teflon, or some other inert material and should be kept as clean as possible to avoid O_3 loss.

3.5 Two-way valve. This valve (often called a three-way valve) is used to conveniently switch the flow through the photometer cell from zero air (for the I_o measurement) to manifold gas (for the I measurement). The valve is

automatically controlled by automatic photometers. For manually operated photometers, the valve is manually controlled and may be an electric solenoid valve controlled by a switch or a manually operated mechanical valve. In lieu of a valve, the plumbing lines can be manually rerouted each time a new measurement is needed; however, this is quite inconvenient because a number of repetitive measurements of I_o and I are normally taken for each concentration assay.

3.6 Temperature indicator. This indicator is needed to measure the temperature of the gas in the photometer cell in order to calculate a temperature correction. In most photometers, particularly those whose cell is enclosed inside a case or housing with other electrical or electronic components, the cell operates at a temperature somewhat above ambient room temperature. Therefore, it is important to measure the actual temperature of the cell, not room temperature. Ideally, the temperature of the gas inside the cell should be determined. For thin metallic cells, however, measurement of the external cell wall temperature may be sufficiently accurate for practical purposes. Good results have been obtained by simply taping an ordinary certified mercury laboratory thermometer to the cell. However, reading such a thermometer inside enclosures or with covers in place may be difficult or impossible. Hence, a small thermocouple or thermistor connected to an external readout device may be the best approach. The thermocouple may be welded, or the thermistor glued, to the cell wall or even inserted through the cell wall to measure interior cell temperature. In locating the point of temperature sensing, attempt to select a point which is representative of the average cell temperature. For example, one end of the cell may be close to the source lamp and thus somewhat warmer than other parts of the cell. A thermocouple or thermistor temperature indicator should be occasionally checked against a certified thermometer or other temperature standard to insure accurate temperature readings.

3.7 Barometer or pressure indicator. The barometer or pressure indicator is needed to measure the pressure of the gas in the cell in order to calculate a pressure correction. Most photometer cells operate at atmospheric pressure

Thus, if there are no restrictions between the cell and the output manifold, the cell pressure should be very nearly the same as the local barometric pressure, and a certified local barometric pressure reading can be used for the pressure correction. If the cell pressure is different than local barometric pressure, some means of accurately measuring the cell pressure (such as a manometer, pressure gauge, or pressure transducer) is required. Any such device should be calibrated against a suitable pressure standard to insure accurate pressure measurements.

4. Reagents

4.1 Zero air. Zero air can be obtained either from compressed gas cylinders or from ambient air. Since appreciable volumes of air are required, there may be practical limits to the use of cylinder air. When the source of zero air affects the output of a transfer standard, special consideration is needed; see McElroy (1979).

As required by the procedure, zero air must be free of O_3 and any other substance that might react with O_3 (e.g., NO, NO_2, various hydrocarbons, and particulates). Air from any source must be purified to remove such substances. Very dirty air may require a pre-cleaning process to remove large particles, oil mist, liquid water, etc. The primary purification process is based on mechanical and chemical filtering. While various schemes may be acceptable, systems similar to the following have been used successfully: The air is first dried with a Perma-Pure type dryer followed by a column of indicating silica gel. The air is then irradiated with a UV lamp to generate O_3 that converts existing NO to NO_2, and a large column of activated charcoal removes NO_2, O_3, hydrocarbons, and various other substances. If desired, molecular seive can be included for good measure. A final particulate filter removes particulates which can originate in the scrubber columns. The removal of moisture may not be necessary, but fewer problems seem to be encountered when dry air is used.

2. STEP-BY-STEP DISCUSSION/Reagents

The particulars of air purification are not well known, so some experimentation may be necessary to determine the appropriate size or volume for scrubber columns. Also, the capacity of the scrubber materials may not be accurately known, so frequent replacement or renewal of these materials is advisable. Additional information on air purification is available (APHA Intersociety Committee 1977, Section 20, Part I).

A very important requirement in photometer operation is the need for the zero air supplied to the photometer during the I_o measurement to be obtained from the same source as that used for generation of O_3. The impurities present in zero air from different sources can significantly affect the transmittance of an air sample. This requirement presents no problem if the configuration shown in Figure 1 of Appendix A is used. However, there may be problems in certifying transfer standards that have their own sources of zero air. This situation is discussed in more detail in McElroy (1979).

5. Procedure

5.1 General operation. As noted in the procedure, a photometer used for calibration must be dedicated exclusively to calibration service and specifically not used for ambient monitoring. The reason for this requirement is that the photometric readings are used to assay the O_3 standards to be used for calibration, and thus the photometer must be intrinsically accurate. If the photometer is used for ambient monitoring, the cell will eventually become dirty. A dirty cell can lead to O_3 losses and erratic readings, which result in loss of accuracy. Reserving the photometer for calibration where only clean, filtered gas passes through the cell will minimize this loss of accuracy.

O_3 analyzers to be calibrated are normally located at various widely separated field sites. While a UV photometer and the photometric calibration procedure can certainly be used at each field site to calibrate such analyzers,

a number of advantages may be realized by locating a single UV photometer at a central laboratory where it can remain stationary, be protected from the physical shocks of transportation, be operated by a responsible analyst under optimum conditions, and serve as a common standard for all analyzers in a network. Under this concept, the central photometer is used to certify one or more O_3 transfer standards which are carried to field sites to calibrate the O_3 monitors. The advantages as well as inevitable disadvantages of this concept are discussed in McElroy (1979), which also provides helpful information and guidance in the use of O_3 transfer standards.

5.2 Preparation. Since the accuracy of the calibration standards obtained by this procedure depends entirely on the accuracy of the photometer, it is very important to insure that the photometer is operating properly and accurately. The fact that the photometer makes a ratio measurement (i.e., I/I_o) rather than an absolute measurement eases this task. The checks described in this section, if carried out carefully, provide reasonable confidence that a photometer having the required inherent capability is operating adequately.

A well designed and properly built photometer is a precision instrument; once shown to operate adequately, it will likely continue to do so for some time, particularly if the photometer is stationary and used intermittently under ideal laboratory conditions. Thus, the performance checks may not necessarily have to be carried out each time the photometer is to be used. The actual frequency of the checks is a trade-off between confidence in the photometer performance and the cost and effort to carry out the checks, and is thus a matter of judgment. One reasonable approach suggested by the procedure is to carry out the checks very frequently with a new photometer, keeping a chronological record of each performance check (similar to a quality assurance control chart). If the record of the photometer performance shows continued adequacy and reliability, the frequency of the checks can be reduced and still maintain adequate confidence in the photometer. (On the other hand, the record

may indicate the need for continued frequent verification of the system condition.) Even where the record shows excellent stability, the checks should still be carried out at some minimum frequency (e.g., once every 3 or 4 weeks) because the possibility of malfunction is always present. A regular schedule of checks will avoid the risk of losing long periods of data due to photometer malfunction.

5.2.1 Instruction manual: If the photometer is a commercially manufactured one, it should include an operation/instruction manual. This manual should be studied thoroughly and its recommendations followed carefully and completely. If questions arise or problems are encountered, assistance is available from the manufacturer or, if necessary, from an EPA technical assistant.

5.2.2 System check: A visual inspection of the photometer system should be conducted to verify that the system is in order. The configuration and plumbing connections are first compared to the flow diagram. All connections are verified to be sound and not restricting the flow. Any obvious or possible leaks are corrected. Cleanliness of cells, manifold, and lines is checked. A more thorough check for leaks follows this visual inspection. One method is to block the output ports and measure the inlet and outlet flow with an external flowmeter. One can also measure the outlet flow and compare the reading to the system's flowmeter reading. This also serves to check the system's flowmeter. The two-way valve is checked to insure that it doesn't leak. Flowrates and vents are checked for lack of back pressure. The zero air supply components should be serviced periodically by replacing or renewing consumables and by checking or replacing filters.

5.2.3 Linearity test: Because the required photometric measurement is a ratio measurement, a linearity check of the photometer is a good indication of accuracy. The photometer operates over a very narrow range of absorbance,

so nonlinearity is unlikely. Unless the manufacturer has demonstrated or guaranteed a photometer linearity error of less than 3%, however, the user should carry out a linearity test.

A linearity test is conducted by first generating and assaying an O_3 concentration near the upper range limit of the system (probably 0.5 or 1.0 ppm). Then the concentration is diluted with a configuration similar to that shown in Figure 2 of Appendix A. A flow of zero air is added to the original generated concentration, and the mixture is passed through a mixing chamber to insure a homogeneous concentration at the output manifold. For this test, the dilution ratio, R, must be accurately known; hence the flowrates F_O and F_D must be accurately measured to ≤2%. To help insure accurate flow measurements, the two flowmeters should be of the same general type and one should be standardized against the other. The dilution ratio is calculated as the flow of the original concentration (F_O) divided by the total flow ($F_O + F_D$):

$$R = \frac{F_O}{F_O + F_D}$$

With stable, high resolution flowmeters and careful work, R should be accurate to ≤1%.

When F_D has been adjusted and R has been calculated, the diluted concentration is assayed with the photometer. The diluted assay (A_2) is then compared with the original undiluted assay (A_1) by calculating the percent linearity error according to Equation 3 in Appendix A. This linearity error must be less than 5% and should be less than 3% for a well performing system. Note, however, that the result is not really the true linearity error because it includes possible errors in the flow measurements; the test serves only as an indicator. If the linearity error exceeds 5% or is greater than expected,

the accuracy of the flow dilution should be checked and verified carefully before the photometer is assumed to be inaccurate. The test should be carried out several times at various dilution ratios, with an averaging technique used to determine the final result. If any modifications to the UV system are necessary in performing the linearity test, care should be exercised to avoid introducing leaks or other adverse effects.

If the linearity error is excessive and cannot be attributed to flow measurement inaccuracy, then the photometer system should be checked for:

1. dirty or contaminated cell, lines, or manifold;
2. inadequate "conditioning" of system (see paragraph 3);
3. leaking two-way valve or other leak in system;
4. contaminant in zero air;
5. nonlinear detectors in the photometer;
6. faulty electronics in the photometer.

Also, UV system nonlinearity might be indicated when a nonlinear calibration curve is obtained for an analyzer that is expected to be linear.

5.2.4 Intercomparison: A good check on the overall accuracy of a photometric calibration system is occasional comparison with O_3 standards from other (independent) organizations. Such comparisons can be either direct or, where the photometer system is stationary, by means of transfer standards; see McElroy (1979). If both organizations' standards agree, it is very likely that both are accurate. Where two organizations' O_3 standards do not agree, it may not be readily apparent which organization's standard is inaccurate. Nevertheless, the discrepancy indicates that at least one of the systems is inaccurate and that further investigation is needed. Where possible, comparison with an agency engaged in quality assurance may be particularly advantageous, because of the usually greater authority of its O_3 standards.

5.2.5 Ozone losses: In spite of scrupulous cleaning and preconditioning, some O_3 may inevitably be lost upon contact with photometer cell walls and gas handling components. Any significant loss of O_3 must be quantitatively determined and used to correct the output concentration assay accordingly. In any case, loss of O_3 must not exceed 5%.

Possibly the best way to determine O_3 loss, after exhausting all possibilities of minimization, is as follows: First, a stable O_3 analyzer is calibrated with the UV calibration system, assuming no losses. An O_3 concentration is then generated and measured with the analyzer as closely as possible to the actual inlet of the photometer cell. Similarly, the concentration is measured as closely as possible to the outlet of the cell. Each measurement may need to be repeated several times to obtain a reliable average. The tests should be repeated at several different concentrations of O_3. The concentration at the output manifold is also measured. Some disassembly of plumbing fittings is usually necessary for these O_3 measurements, as the best locations for the measurement points are at the inlet and outlet fittings of the photometer cell. For convenience, access fittings may be permanently installed at these points to facilitate frequent loss checks.

Since a continuous flow of O_3 through the photometric system is required when making the measurements, the two-way valve must be in the "sample" position. In systems with manually controlled valves, this presents no problem. In systems with automatically controlled valves, some means of maintaining a continuous flow of O_3 into the absorption cell is necessary.

In making these measurements, it is important to avoid shock or damage to the photometer and to reassemble the fittings properly and check for the absence of leaks. Also, any pressure differences at the measurement points may cause inaccurate measurements if the analyzer is affected by pressure changes.

2. STEP-BY-STEP DISCUSSION/Procedure

For the configuration shown in Figure 1 of Appendix A, the percent O_3 loss is calculated as

$$\text{Percent } O_3 \text{ loss} = \frac{R_m - \frac{1}{2}(R_{in} + R_{out})}{R_m} \times 100\%$$

where R_{in} is the O_3 concentration measured at the cell inlet, R_{out} is the O_3 concentration measured at the cell outlet, and R_m is the O_3 concentration measured at the output manifold.

For other configurations, the percent loss may have to be calculated differently. The O_3 loss correction factor for use in Equation 4 of Appendix A is calculated as

$$L = 1 - 0.01 \times \text{percent } O_3 \text{ loss}$$

5.3 Assay of O_3 concentrations.

5.3.1 Photometers use lamps and electronic circuits which generate some heat, and therefore most photometers will experience some temperature rise from room temperature. It may be important to the stability and hence accuracy of the photometer to wait until thermal equilibrium has been reached. The process cannot usually be hastened. Thus, the system should be turned on sometime before it is needed to allow adequate stabilization time. Since the stabilization time may vary considerably from one photometer to another, this may be a consideration when selecting a portable photometer for field calibrations.

5.3.2 It is very important that the photometer not drift between the I_o and I measurements. Therefore, these two measurements should be as close together in time as possible. However, delay between the two measurements is needed to allow the cell to flush completely before the second measurement. Thus cell flowrate is an important consideration. About 5 cell volumes should

pass through the cell to adequately flush it. To keep the flush time down to 10 seconds or less, the cell flow needs to be ≥30 cell volumes/minute. With a cell volume of 30 cm^3, a flow of 2 liters/minute will provide 5 cell flushes in ~5 seconds.

5.3.3 The flowrate into the output manifold must be greater than the sum of the flowrates of the device or devices connected to the manifold. When the flows are adjusted, it is a good idea to check the vent to make sure that sufficient vent flow exists to prevent entry of ambient air.

5.3.4 Similarly, F_z must be adjusted to exceed the photometer cell flowrate, and the F_z vent should also be checked for adequate flow to assure no possibility of ambient air entry.

5.3.5 The photometer is first checked by allowing it to assay a zero O_3 concentration (zero air). Needless to say, if the photometer does not indicate that $I = I_o$, something is wrong. If this happens, perhaps the most obvious thing to check is whether the manifold is really at zero concentration. Sometimes the O_3 generator continues to generate small amounts of O_3 even when it is supposed to be off. This can be checked by supplying zero air directly to both inlets of the two-way valve, bypassing the O_3 generator. If the photometer still fails to give the same reading, the fault is somewhere in the photometer, which must be checked and corrected. A very small difference between I and I_o is perhaps tolerable.

Note here that many commercially available photometers operate automatically. In this type of photometer, the two-way valve is an integral component and is controlled automatically by the photometer control system. Also, automatic photometers generally cycle through the entire operational sequence continuously and output a single measurement of the I/I_o ratio rather than individual I and I_o measurements. In fact, the output reading will probably be scaled in actual concentration units rather than an I/I_o ratio.

5.3.6 The O_3 generator is adjusted to produce an O_3 concentration as needed. Usually, the first concentration is near the upper range limit, about 0.45 or 0.9 ppm, as appropriate. It is important to allow plenty of time for the O_3 generator to stabilize at this setting and for the entire system to "condition" to this concentration of O_3.

5.3.7 The two-way valve is actuated to sample zero air. It is important to allow sufficient time to thoroughly flush the photometer cell and to obtain a stable reading. The I_o value is measured and recorded.

5.3.8 The two-way valve is actuated to sample the O_3 concentration. Again, it is important to allow sufficient time for cell flushing and for a stable reading. The I value is measured and recorded. Automatic photometers perform this and the previous step automatically.

5.3.9 The temperature and pressure of the sample in the photometer cell are recorded. Because conditions inside the cell may be different than ambient (room) conditions, one must try to measure the actual temperature and pressure. Paragraphs 3.6 and 3.7 (above) present a discussion of these parameters and their measurement.

5.3.10 Equation 4 in Appendix A is used to calculate the O_3 concentration. An average of several photometer readings should be used, as there is typically some variation in the readings. With automatic photometers, this is no problem because operation is continuous and new readings are outputted after each cycle. For manually operated photometers, Steps 5.3.7 and 5.3.8 have to be repeated several times.

Equation 4 in Appendix A translates the photometer absorption readings for I and I_o into O_3 concentration in parts per million. The first term is the primary Lambert-Beer relationship. The second and third terms are for

temperature and pressure corrections, respectively. The last term is the conversion factor to parts per million and also includes the correction for O_3 losses in the system.

Each symbol used in the equation is explained below the equation. Note that the absorption coefficient is given for a temperature of 0° C, so the temperature correction term is important and cannot be neglected.

The optical pathlength of the photometer cell needs to be known very accurately (±0.5%). If the photometer's operation manual does not indicate the exact pathlength, the cell will have to be measured; some disassembly of the cell may be required to do this. In purchasing a photometer, it might be wise to insist that the manufacturer provide this information.

The correction factor for O_3 losses, L, is discussed under paragraph 5.2.5.

Since the photometer readings I and I_o are treated as a ratio (I/I_o), the units (which are identical) are not important. The calculation of the natural logarithm (symbol "ln") of the I/I_o ratio can be carried out by means of a table of natural logarithms or with a calculator that has natural log capability. Many small pocket calculators have an "ln" key for this purpose. Be sure to compute the <u>natural</u> logarithm and not the base 10 logarithm (symbol "log") which would give an incorrect result. However, if your calculator has base 10 (log key) logarithms but not natural logarithms (ln key), Equation 4 in Appendix A can be rewritten as

$$[O_3]_{OUT} = (-1/\beta\ell \log I/I_o)(T/273)(760/P)(10^6/L)$$

where $\beta = 134\ atm^{-1}cm^{-1}$.

2. STEP-BY-STEP DISCUSSION/Procedure

Automatic photometers may automatically evaluate all or part of Equation 4 in Appendix A. Usually, the photometer evaluates the first term and the remaining terms — corrections for temperature, pressure, and O_3 losses — have to be applied manually. Caution: some photometers may be set to evaluate the first term of Equation 4 in Appendix A based on a temperature other than 0° C, in which case the "273" in the temperature term would have to be replaced by the proper temperature.

Some automatic photometers use a linear approximation rather than the logarithmic form for the first term of Equation 4 in Appendix A. For a pathlength of ~70 cm, this results in an error of ~1% at an O_3 concentration of 1 ppm. For longer pathlengths, the error becomes more severe. At concentrations of less than 0.5 ppm, the error is less than 0.5% and can probably be ignored. But at higher concentrations or longer pathlengths, the error may become significant, in which case the error must be determined and an appropriate correction applied to the resultant concentration.

5.3.11 Additional O_3 concentration standards are obtained by repeating the appropriate steps between 5.3.6 and 5.3.10 or by Option 1, which is discussed later.

5.4 Certification of transfer standards. All transfer standards must be certified (related) to primary O_3 concentration standards using this calibration procedure. Transfer standards that assay O_3 concentrations generated externally can be certified very similarly to the calibration of an O_3 analyzer. But special arrangements must be made for transfer standards which include their own source of O_3. All of these matters are discussed in McElroy (1979).

5.5 Calibration of ozone analyzers. The ozone analyzers designated here are ambient monitors installed at field monitoring sites. Ambient monitors are normally calibrated <u>in situ</u> without disturbing the normal sampling setup,

except for transferring the sample inlet from the ambient sampling point to the calibration system. The steps in Section 5 of the procedure should be followed regardless of whether the ambient monitor is being calibrated directly by the photometric calibration procedure or by means of a transfer standard.

5.5.1 Warm-up: Before calibration, a newly installed O_3 analyzer should be operated for several hours (preferably, overnight) to permit stabilization. Brand-new analyzers fresh from the factory may require several days of operation to fully stabilize. The photometer or transfer standard must also be allowed an adequate warm-up and stabilization period before use, particularly if stored or transported in cold weather.

5.5.2 In adjusting the analyzer zero, it is important that the input concentration is truly zero (i.e., zero scrubbers recently serviced and in good condition, and O_3 generator off). Remember that O_3 generators sometimes generate small amounts of O_3 even when the mechanical adjustment is in the off position. Zero air obtained from the calibration system rather than from any zero air source internal to the analyzer should be used. After a stable reading has been achieved, the zero on the data recording device (not the analyzer's meter indicator) is adjusted. The data recording device is usually a chart recorder, but if a data acquisition system or other means is used, zero the analyzer according to the indication of the data system or other device. When using a chart recorder (or other device which cannot read below zero), an offset zero — 5% of scale is convenient — insures a "live" zero (i.e., the recorder can respond to either an increase or decrease in the zero base line).

5.5.3 An O_3 concentration standard of ~90% of the range of the analyzer to be calibrated — ~0.45 or ~0.9 ppm for the 0.5 and 1.0 ppm ranges, respectively — is generated. If the photometric calibration procedure is being used, this concentration standard is determined according to Steps 5.3.6 through 5.3.10. When a transfer standard is used, the concentration is determined by

reference to the transfer standard's certification relationship (with applicable corrections if necessary); see McElroy (1979).

5.5.4 When the analyzer reading has stabilized, the analyzer's span control is adjusted to provide a convenient scale factor. An offset zero (if used) must be taken into account according to Equation 5 in Appendix A. Also, the span and zero controls may be interrelated, so if the span adjustment is large, the zero adjustment (Step 5.5.2) should be repeated, which requires that the span adjustment (Step 5.5.4) also be repeated.

5.5.5 A complete calibration includes five or more upscale calibration points, so additional O_3 concentration standards need to be generated and sampled by the analyzer. The additional concentrations may be generated either by adjusting the O_3 generator or by Option 1 (discussed later). After the span adjustment on the first concentration, no further adjustments to the span control are made. The additional concentrations should be approximately evenly spaced over the scale range of the analyzer. The analyzer response to each concentration is recorded together with the concentration.

5.5.6 The concentrations and associated analyzer responses are plotted on graph paper and connected with a smooth line to form the analyzer calibration curve. For linear analyzers, the line should be straight. If possible, the line should be determined by least squares regression and plotted according to the calculated slope and intercept. After establishment of the calibration curve, the span control should be locked, if possible, and not adjusted until the next calibration. The calibration curve is then used (either visually or by calculation) to translate all subsequent analyzer measurements to concentration units until the time of the next calibration.

If zero and span checks are going to be used to check the analyzer between calibrations, a zero and span check should be carried out immediately following

the calibration. The readings thereby obtained become reference readings which are compared to subsequent zero and span checks to detect possible analyzer drift.

5.5.7 Option 1: Instead of adjusting the O_3 generator to obtain various O_3 concentration standards, such standards may be obtained by dilution of a high standard with zero air. This option obviates the need for an adjustable O_3 generator but requires additional apparatus to effect the dilution, as shown in Figure 2 of Appendix A. Note that a mixing chamber is required to insure thorough mixing of the two gas streams. Since the diluted concentration standards are calculated based on the dilution ratio, accurate flow measurements of both the primary O_3 generator flow (F_O) and the dilution flow (F_D) are required. Also, since the total flow may be increased substantially, verify:

1. that the zero air supply and purification system can adequately handle the extra flow;
2. that the pressure in the manifold or in the O_3 generator does not increase significantly due to increased back pressure at the manifold vent;
3. that the flow through the O_3 generator (F_O) does not change and thereby cause a change in the original (undiluted) O_3 concentration.

Equation 6 of Appendix A is used to calculate the diluted O_3 concentrations.

SECTION 3

OBTAINING A PHOTOMETER

This section discusses some of the considerations to be addressed if one wishes to construct a photometer suitable for the assay of sub-ppm O_3 concentrations in clean systems. It also describes commercially available photometric systems.

CONSTRUCTION OF A PHOTOMETER

Successful construction of a photometer for O_3 assay requires a clear understanding of the parameters to be measured and the magnitude of the error in concentration resulting from each error associated with mismeasurement of different parameters.

Reviewing the basic photometric equation from Section 1,

$$T = \frac{I}{I_o} = e^{-\alpha c \ell}; \quad c = \frac{-1}{\alpha \ell} \log \frac{I}{I_o} = \frac{A}{\alpha \ell}$$

it should be clear that there are four parameters (I, I_o, α, and ℓ) which must be determined to calculate the concentration, c. The value of α is obtained from a review of the literature and is 308 $atm^{-1}cm^{-1}$. This absorption coefficient is considered accurate to ±1.5% when applied to O_3 at 254 nm and STP (0° C and 760 torr). When assaying O_3 at temperatures and pressures other than STP, the temperature and pressure of the sample must also be measured to permit proper calculation of the concentration.

3. OBTAINING A PHOTOMETER/Construction

From Section 1,

$$\frac{dc}{c} = - \frac{d\alpha}{\alpha}$$

Thus, a given error in α causes a multiplicative error in c of the same magnitude but in the opposite direction. That is, if the literature value of α is 1% too large the calculated concentration will be 1% too small. Also, a given error in the pathlength, ℓ, causes the same kind of error in c as does an error in α.

The transmittance, T, is the parameter which must be measured with the greatest precision, because the error in T is multiplied by the term 1/lnT:

$$T = e^{-\alpha c \ell}$$

$$\frac{dc}{c} = - \frac{dT}{T \ln T}$$

For T = 0.98, this term is ~50; for T = 0.997 (100 ppb O_3; 1 m path) the term increases to ~325. Thus, for T near 0.997, one must measure T with more than 300 times the relative accuracy of the measurement of α or ℓ in order to keep the error in c to the same level as that caused by the errors in α and ℓ. Also, note that the inaccuracy caused by errors in T depends strongly on the concentration (i.e., value of T), whereas errors caused by mismeasurement of α and ℓ are constant multiplicative factors. For typical values of ℓ of 1 and 2 m, the respective values of T (assuming c = 500 ppb) are 0.984718 and 0.969669. If the photometer can determine T with an error of 5 parts in 10^5, the respective errors in c are 0.3297% and 0.1674%.

Measurement of T is related to many (often conflicting) design features. For example, increasing ℓ decreases T so a given error in T causes a lesser error in c. However, increasing ℓ generally leads to a longer instrument

cycle time (due to the increased time period required to flush the longer cell); the longer cycle time allows more electronic drift and thermal effects so that the error in T generally increases. Attempting to flush the cells faster also leads to greater error in T due to scintillation from turbulence in the gas. Decreasing the cell diameter leads to a shorter flush time but also a less favorable surface-to-volume ratio, and O_3 losses may become a significant problem.

The precision in the measurement of T is generally limited by the electronic and mechanical stability of the photometer. Therefore, the photometer designer should attempt to use a rather short instrument cycle time (10 seconds to a minute or so) in order to minimize these drifts. As an example of the kind of problem one might encounter while examining instrumental drifts, consider the effects of a detector whose sensitivity changes by 2% per month (a large but not-unheard-of drift):

$$2\%/\text{month} = \frac{2\%}{\text{month} \times 30\ \text{days/month} \times 24\ \text{hours/day}} = \frac{0.0028\%}{\text{hour}} \simeq \frac{0.001\%}{20\ \text{minutes}}$$

System drift due to the effects of one detector is 1 part in 10^5 in ~20 minutes. Clearly, if the design goal is to measure transmittance to 1 part in 10^5, the instrument cycle time will have to be much shorter than 20 minutes, because a typical photometer includes more than one detector as well as some amplifiers and voltage-to-frequency converters contributing to electronic drift.

In order to obtain O_3 measurements of the highest accuracy, it is important that the photometric system operate at a single wavelength (i.e., the system should be monochromatic). Although the problem is not widely discussed, many photometric systems used to measure O_3 concentration utilize some rather fortuitous circumstances to achieve a (near) monochromatic photometer. The low pressure mercury source emits radiation at a number of wavelengths other than 254 nm. This can lead to at least two problems. The 185 nm radiation

from the source can produce O_3 in the photometer cells (indeed, it is this radiation which is used to produce O_3 in most photolytic O_3 generators). Wavelengths which may ordinarily not produce O_3 but are sensed by the detector system cause errors unless the absorption coefficient for O_3 is the same at these wavelengths as at 254 nm.

In practice, one can construct a photometer which minimizes these problems. Use of a Vycor envelope on the source will filter out the 185 nm radiation, since Vycor has a very low transmittance at 185 nm. Use of solar-blind detectors eliminates interferences from radiation of wavelengths greater than about 300 nm. In the 200 to 300 nm region passed by the Vycor and sensed by the detectors, the mercury source has a dozen or so lines. Of these lines, the 254 line is on the order of 100 times stronger than any other line. Reasonably careful calculations of the effect of using a less than ideally monochromatic system indicate that one can expect to underestimate the O_3 concentration by ~0.5%. Limited attempts to measure the effect produced results of 0.5 ± 0.5% (Paur and Ellis, unpublished data).

Another area of design which can greatly affect the precision of photometric measurements involves signal processing to eliminate or reduce electrical noise picked up in signal cables. In modern instrumentation this problem is often addressed by use of current-to-frequency circuitry that converts the detector current to a digital frequency very early in the signal processing process. The digital frequency is relatively immune to extraneous noise because the counters or digital integrators only need to discriminate between the presence or absence of a pulse rather than trying to measure the amplitude of a d.c. signal with a precision of 1 part in 10^5.

3. OBTAINING A PHOTOMETER/Construction

The intensity of the 254 nm radiation from low pressure mercury sources is very sensitive to the temperature of the source. Even though a photometer typically uses a reference detector to monitor the source intensity, the precision of the transmittance measurement can generally be significantly improved by maintaining the source at a constant temperature. The temperature is typically in the 45 to 50° C range, since the source is generally some 4 to 6 times brighter when operated at 50° C than when operated at 20° C.

It is useful to design the source holder, detector holder, amplifier, and voltage-to-frequency converters into a package that is thermostated to a constant temperature. Ideally, the detectors and electronics should operate at less than 50° C; however, solar-blind photodiode detectors typically have low dark current even at 50° C, and almost all modern electronic components are specified to at least 70° C.

As indicated in Section 2, the material of construction is of considerable importance because O_3 is relatively easily decomposed by contact with most materials. The materials most commonly used are glass and Teflon or other fluorocarbon materials like Kynar. Some metal surfaces such as aluminum may eventually be passivated, but use of such materials is generally considered to be quite detrimental to the reliability of the measurements. (Some metals, such as hot copper turnings, make excellent O_3 scrubbers and can be used to destroy O_3 from laboratory apparatus before discharging vent gases to the atmosphere.)

Although the O_3 generator is not part of the photometer, the reader is cautioned to independently characterize the O_3 generator so that generator instability will not be interpreted as instability in the O_3 measurement system.

COMMERCIALLY AVAILABLE PHOTOMETRIC SYSTEMS

Dasibi Ozone Analyzer (Models 1003-AH and 1003-PC)

The Model 1003-AH differs from the Model 1003-PC only in that the latter includes a self-contained O_3 generation system; both will be referred to as "Model 1003." It is important to distinguish among three different uses of the Dasibi Model 1003 O_3 analyzer. These are discussed below.

Ambient Ozone Monitor--

This Technical Assistance Document specifically does not address the use of the Dasibi O_3 analyzer for measurement of ambient O_3.

"Transfer Standard" for Ozone Monitor Calibration--

When used as a transfer standard, the Dasibi O_3 analyzer is periodically certified in the laboratory and is assumed to give stable results between certifications. The analyzer is taken to field sites and used to determine the O_3 concentration in a calibration system during calibration of the field O_3 monitor. Since the Dasibi analyzer is operating in a clean system, the possibility of interference is significantly reduced. This document provides limited information on use of Dasibi analyzers as transfer standards; see also McElroy (1979).

Photometer--

The Dasibi Model 1003 O_3 analyzer is easily modified to operate as a photometer which measures the relative transmittances of two gas samples at 254 nm. If one gas sample is zero air and the second sample contains O_3 in zero air, the concentration of O_3 in the latter sample can be readily calculated from the measured transmittance of the sample, the known absorptivity of O_3 at 254 nm, and knowledge of the optical pathlength through the sample. It is this last use of the Dasibi Model 1003 O_3 analyzer — its use as a convenient hardware package for making photometric measurements at 254 nm — that is of interest here.

3. OBTAINING A PHOTOMETER/Commercially Available Systems

In order to help the reader appreciate the significance that O_3 measurements carried out using a Dasibi photometer have for the photometric technique in general, some of the important details of the Model 1003 hardware will be described.

The Dasibi instrument uses a low pressure mercury discharge lamp as its light source. The 185 nm O_3-producing radiation is blocked by means of a Vycor shield around the lamp. The solar-blind vacuum photodiode detectors do not respond to radiation of wavelengths greater than about 300 nm. The source-detector combination thus produces an effectively monochromatic photometer operating at the 254 nm Hg line.

The Dasibi is a two channel photometer system (see Figure 3-1). One detector (sample channel) monitors the intensity of 254 nm radiation passing through the absorption cell. A second detector (control channel) positioned near the UV source views a fraction of the 254 nm radiation. This second detector functions as an energy monitor and is used to compensate for changes in source intensity.

The electrometers are current-to-frequency converters; signals from the detectors are converted to digital signals very early in the signal processing and are thereby protected from further degradation. The digitized signals are fed into a patented counting system which also controls a solenoid valve allowing either zero air or sample air to pass through the absorption cell.

During an instrument cycle, the solenoid valve directs zero air into the absorption cell and flushes the cell ~2.5 times (~5 seconds with ~2 liters/minute of air passing through a 66 cm^3 cell). Two independent counters are actuated first in a count-up mode. The control counter digitally integrates the intensity of light entering the control channel while the sample counter integrates the light intensity emerging from the sample cell. Both counters are stopped simultaneously when the sample channel counter reaches a preset span number. The solenoid valve is switched to direct sample air into the

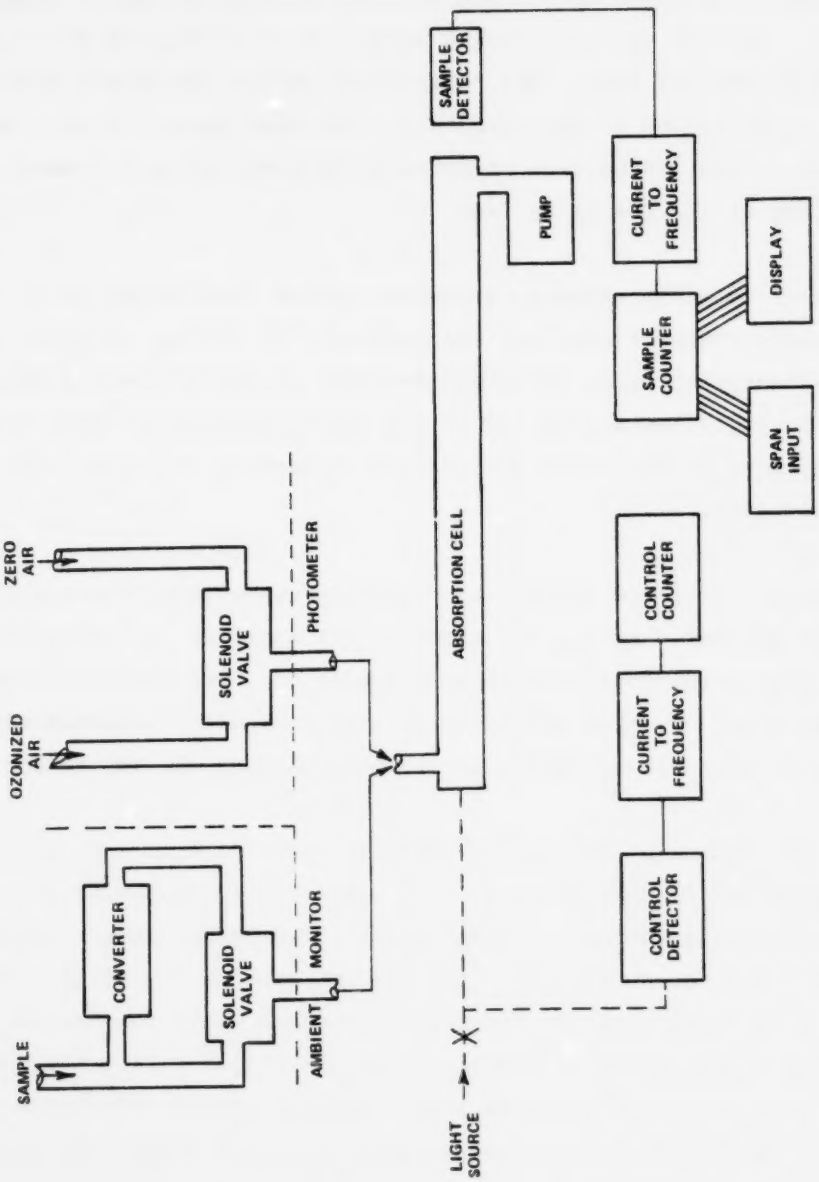


Figure 3-1. Simplified block diagram of Dasibi Model 1003 Ozone Analyzer.

absorption cell, which is flushed for ~5 seconds. The counters are then activated in a count-down mode. When the control channel counter has accumulated the same number of counts as it did during the zero reference part of the cycle (i.e., when the control counter has counted down to zero), both counters are stopped. The count remaining in the sample counter represents the quantity $I_o - I$ and is shifted into the instrument output display.

The Dasibi Model 1003 uses the linear approximation of the absorption equation to convert the measured transmittance to a concentration:

$$\frac{I}{I_o} = 1 - \alpha c \ell$$

$$I = I_o - I_o \alpha c \ell$$

$$I_o - I = I_o \alpha c \ell$$

Since the Dasibi uses current-to-frequency signal processing, I_o can be assigned an arbitrary value, and the measurement period can be adjusted to allow the sample counter to reach the value of I_o. Dasibi chose a value of I_o such that at 1.0 ppb O_3 the difference between I_o and I would be 10 counts. At 1.0 ppb ozone

$$I_o - I = 10 \text{ counts} = I_o \alpha c \ell$$

$$I_o = \frac{10 \text{ counts}}{\alpha c \ell}$$

where $\alpha = 308.3 \text{ atm}^{-1}\text{cm}^{-1}$ at STP (273 K and 760 torr), base e
$= 277.6 \text{ atm}^{-1}\text{cm}^{-1}$ at 300 K (27° C) and 752 torr

$\ell = 71$ cm

$c = 10^{-9}$ atmosphere or 1.0 ppb

Thus, $I_o = 456{,}844$ at STP
$= 507{,}367$ at 300 K and 752 torr

This value of I_o is the span number one would use for a Dasibi photometer operated at 300 K and 752 torr, and it can be loaded into the instrument via front panel switches. On older Dasibi Model 1003 instruments (those without zero offset capability), the span number can be loaded with 4-digit accuracy (e.g., 507400); on current production Model 1003 instruments (those with zero offset capability), only 3-digit accuracy is obtainable (507000). With the front panel mode switch in the span position, this span number is displayed as 50.40 on the older instruments and 50.750 on the current instruments. The added 00.050 on the current instruments occurs because of the zero offset circuitry.

The actual span number to use in a Dasibi photometer for an actual set of operating conditions is conveniently obtained by multiplying the span number derived for STP by the appropriate ratios of the actual operating temperature and pressure to the STP values:

$$\text{Span No. (T,P)} = \text{Span No. (273 K, 760 torr)} \times \frac{760}{P} \times \frac{T}{273}$$

$$\text{Span No. (300 K, 752 torr)} = 45.684 \times \frac{760}{752} \times \frac{300}{273}$$

$$= 50.736 \text{ or } 50.740 \text{ for older instruments}$$
$$50.750 \text{ for newer instruments}$$

When an actual span number is loaded into the Dasibi instrument, subsequent displayed O_3 concentrations are accurate only to the extent that the operating temperature and pressure remain constant. Thus a 3° C change in temperature would introduce a 1% error, and a 7.5 torr change in pressure would have a similar effect. In most cases, only minor fluctuations in operating conditions occur; these are generally ignored. When significant changes occur or better accuracy is desired, the indicated Dasibi reading can be corrected by measuring the actual operating temperature and pressure at each measurement and using the following equation:

$$[O_3]_{Corr} = [O_3]_{Ind} \times \frac{45.684}{\text{Span No.}} \times \frac{760}{P} \times \frac{T}{273}$$

where Span No. = span number loaded into Dasibi instrument
T = actual operating temperature (K)
P = actual operating pressure (torr)

For convenience, the STP span number (45.684) may be left in the instrument, allowing the second term on the right of the above equation to drop out.

Use of the linear form of the absorption law in the Dasibi instrument results in a small, readily calculable error in the displayed concentration. A display value of 1 ppm ($I_o - I$ = 10000 counts) in the Dasibi using a span number of 50.740 corresponds to a measured transmittance of

$$T = \frac{I}{I_o} = \frac{I_o - (I_o - I)}{I_o} = \frac{507400 - 10000}{507400} = 0.980292$$

The concentration calculated from the transmittance using the exponential form of the absorption law is 1.010 ppm; thus the linear absorption law causes an error of 1.0% at 1 ppm. The error decreases at lower concentrations. At 0.5 ppm, the error is 0.5%.

The precision of the photometer is more than adequate for calibration of ambient O_3 monitors. One standard deviation of 10 consecutive measurements is typically on the order of 1 ppb. This means the instrument has a precision in the transmittance measurement of ~1 part in 50,000.

Modification of the Dasibi Model 1003 Ozone Analyzer--

The Dasibi Model 1003 O_3 analyzer was designed as an ambient O_3 monitor. To provide a reference gas for the reference part of the instrument cycle, the field instrument employs a converter which, ideally, removes all of the O_3 from an ambient air sample without causing any other changes in the sample. In order to avoid any question of effectiveness of this converter, it is removed

from the instrument. Zero air is then diverted from upstream of the O_3 generator in the calibration system (self-contained in the Model 1003-PC) and is brought at atmospheric pressure to the reference side of the solenoid valve. It is important that the same zero air used for the generator be provided for the reference part of the cycle: experience has shown that samples of "zero" air from different sources may vary significantly with respect to transmittance at 254 nm.

The sample channel counter is prevented from counting below numerical zero by a reset line which resets the counter to zero as soon as a digital "borrow" signal is generated by the most significant digit of the counter. In order to display the true instrument zero, this reset line (located on the top printed circuit board in the instrument) is disconnected. Note that the first count below zero in an up-down counting system generates an "all 9's" display. For numbers below numerical zero, the displayed value is greater than the actual count by 100.000. Thus a displayed value of 99.992 equals (99.992 - 100.000) or -0.008. In current production models of Dasibi 1003 O_3 analyzers with zero offset capability, it is not necessary to disconnect the reset line provided sufficient positive zero offset is dialed into the instrument via the front panel zero offset switch.

A third modification which may be required on older Dasibi photometers consists of moving the solenoid valve a few centimeters away from the absorption cell. When operated as manufactured, the instruments "zero" ~15 ppb below numerical zero. The amount of this negative zero offset is weakly dependent on the sample flowrate. Since the solenoid valve is immediately adjacent to the absorption cell, it has been postulated that turbulence set up in the solenoid valve is carried into the cell. The turbulence might be different during different parts of the instrument cycle (due to switching of the solenoid valve), and the schlieren effects would change the transmittance of the zero air sample. (Note that the 15 ppb effect corresponds to a change in transmittance of only 1 part in 3300.) Moving the solenoid valve a few centimeters from the absorption cell and connecting it to the cell via a piece

of Teflon tubing appears to allow turbulence patterns set up by the valve to decay before the gas reaches the cell. Making this modification causes the instrument to zero properly (i.e., ~90 percent of the zero readings are within ±2 ppb of zero after the instrument has thoroughly warmed up). In current production models of Dasibi 1003 O_3 analyzers, the solenoid valve is separated from the absorption cell by a short distance. Thus, this third modification may not be required to obtain an instrument zero within a few ppb of numerical zero when using current models of the O_3 analyzer.

Instrumental Sources of Errors--

The Dasibi instruments have at least two sources of error which may not be readily apparent to the operator. The first is partial failure of the solenoid valve. The instrument measures the relative transmittance of a reference gas sample and an ozonized gas sample. If the solenoid valve has a significant leak, the two gas samples are mixed to some degree and the difference in transmittance is reduced. This causes the instrument to indicate lower concentrations than are actually present. Leak-testing the valve is neither difficult nor time-consuming, and should be performed regularly.

A second possible source of error is the dark count from the current-to-frequency converters. To measure the dark count, the light source is removed from the instrument and the sample and control frequencies are displayed. The fractional error in each channel is equal to the ratio of dark count to light count. Unfortunately, if the bias currents in the electrometers result in a net current of opposite polarity to that required to produce a dark count, no count is produced and this simple test for determining the magnitude of the dark count error does not yield the desired information. In the instruments examined, the dark counts were negligible.

Dasibi Ozone Analyzer (Models 1008-AH and 1008-PC)

The Model 1008-AH differs from the Model 1008-PC only in that the latter includes a self-contained O_3 generation system; both models will be referred to as "Model 1008."

3. OBTAINING A PHOTOMETER/Commercially Available Systems

The Dasibi Model 1008 is a commercial photometer designed specifically for use as a primary calibration standard for O_3. This model can also be used as a transfer standard for O_3 monitor calibration (see previous discussion on use of the Dasibi Model 1003 as a transfer standard). It can be used as an ambient O_3 monitor provided it is modified to incorporate an O_3 scrubber in the flow system. However, as of this writing, the Model 1008 has not been designated as an equivalent method for measurement of O_3 in the atmosphere.

The optical subsystem of the Model 1008 is the same as that used in the Model 1003 except for the addition of two sensors, both located at the exit of the absorption cell. An absolute pressure sensor with a range of 0 to 1300 torr and overall accuracy of 2 torr over the range of 500 to 900 torr, and a temperature sensor with a range of 0 to 50° C and overall accuracy of better than 0.5° C are used to measure the pressure and temperature of the sample exiting the absorption cell.

Although the required transmittance measurement is made with the same patented counting technique used in the Model 1003, the electronics subsystem of the Model 1008 is different from that of the Model 1003. The Model 1008 uses a Zilog-80 (Z-80) microprocessor to evaluate the logarithmic form of the absorption equation to convert the measured transmittance of the sample to a concentration:

$$-\ln \frac{I}{I_o} = \alpha c \ell \qquad \text{or} \qquad c(\text{ppm}) = -\frac{10^6}{\alpha \ell} \ln \frac{I}{I_o}$$

The microprocessor calculates the O_3 concentration by using the following parameters: ℓ and 10^6 (conversion factor for atmospheres to ppm), which are stored in the software; the value of α, which can be varied via a 3-digit thumbwheel switch; and the measured transmittance of the sample (I/I_o). The microprocessor then uses the parameters of standard temperature and pressure (273 K and 760 torr), also stored in the software, and the measured temperature and pressure of the sample to calculate the O_3 concentration corrected for

temperature and pressure. Thus, the Model 1008 automatically evaluates all terms in Equation 4 of the O_3 calibration procedure (Appendix A) except for L, the correction factor for O_3 losses. It is the operator's responsibility to determine L and apply the appropriate correction.

When the Model 1008 is used as a primary calibration standard, a value of 308 must be used for the absorption coefficient, α. The Model 1008 has a front panel T/P switch which allows for display of either the corrected or uncorrected O_3 concentration. A front panel function switch can be used to display the sample temperature and pressure. When used in conjunction with the T/P switch, these readings can be used to verify that the Z-80 is making proper temperature and pressure corrections. The unit also has zero offset capability similar to that of the Model 1003.

The Model 1008 is equipped with a "T" between the solenoid valve and the cell inlet and another at the cell exit to facilitate the O_3 loss determination required in the O_3 calibration procedure. On the back of the photometer are inlet ports for zero air and sample. The zero air required for photometer operation should be supplied at slightly positive atmospheric pressure, since the unit does not contain a sample pump.

The Dasibi Model 1008-PC is similar to the Model 1008-AH with the addition of a stable O_3 generator, a manifold, and optional ozonator-photometer feedback circuitry.

Instrumental sources of error are basically the same as those discussed for the Model 1003.

Columbia Scientific Industries Corp. (CSI) Photocal 3000 Ozone Calibrator

The CSI Photocal 3000 O_3 calibrator is designed for two applications, as discussed below.

3. OBTAINING A PHOTOMETER/Commercially Available Systems

"Transfer Standard" for Ozone Monitor Calibration--

When used as a transfer standard, the O_3 calibrator is periodically certified in the laboratory and is assumed to give stable results between certifications. The calibrator is taken to field sites and used to supply accurately known concentrations of O_3 for calibration of the field O_3 monitor. Use of a good quality zero air source is important in calibration. Since the CSI photometer references to the zero air source, the possibility of interference from other UV-absorbing gases is not significant. However, impurities which react with O_3, such as NO, may cause a reduced O_3 output or cause the output to be noisy in O_3 generating systems.

The operation of the calibrator as a transfer standard is essentially the same as that described under "Photometric Calibrator," below; see also McElroy (1979).

Photometric Calibrator--

The CSI calibrator contains an O_3 generation system and a photometer which measures the relative transmittances of two gas samples at 254 nm. The O_3 generator produces O_3 in operator-selected concentrations from 50 to 1000 ppb. The photometer taps off samples of zero air and of O_3 in zero air. The concentration of O_3 in the latter sample can be readily calculated from the measured transmittance of the sample, the known absorptivity of O_3 at 254 nm, and knowledge of the optical pathlength through the sample. Measurement in the zero air serves as a reference. It is this use of the CSI O_3 calibrator, i.e., its use as a convenient hardware package for generating O_3 and making photometric measurements at 254 nm, that is of interest here. Some important details of the CSI hardware are described below.

The instrument uses a low pressure mercury discharge lamp for its light source. The 185 nm O_3-producing radiation is blocked by means of a Vycor shield around the lamp. The solar-blind vacuum photodiode detectors do not respond to radiation at wavelengths of greater than ~300 nm. The source-detector combination thus produces an effectively monochromatic photometer operating at the 254 nm Hg line.

3. OBTAINING A PHOTOMETER/Commercially Available Systems

The Photocal 3000 is a two channel photometer system (see Figure 3-2). One detector (sample channel) monitors the intensity of 254 nm radiation passing through the absorption cell. A second detector (control channel) views a fraction of the 254 nm radiation reflected from the main beam exiting the lamp housing. The control channel functions as an energy monitor and is used to compensate for changes in source intensity.

The electrometer used for the transmission measurement is a current-to-frequency converter; the signal from the sample detector is converted to a digital signal very early in the signal processing and is thereby protected from further degradation. The digitized signals are fed into a microprocessor, which also controls solenoid valves that allow either zero air or sample air to pass through the absorption cell.

During an instrument cycle, the solenoid valves first direct zero air into the absorption cell to flush the cell ~5 times (~10 seconds with ~2.5 liters/minute of air passing through a 82 cm^3 cell). A counter digitally integrates the light intensity emerging from the absorption cell, and the information is stored in memory by the microprocessor. The valves are then switched to direct sample air into the absorption cell and the cell is flushed for ~10 seconds. The integrated light intensity emerging from the cell is again measured.

The CSI photometer uses the exponential absorption equation to calculate the concentration from the measured transmittance. An absorption coefficient of 308 $atm^{-1}cm^{-1}$ at STP (273 K and 760 torr) base e is used in the calculation. The system dark current is automatically measured and subtracted from the signal currents by the microprocessor.

From the Lambert-Beer law,

$$I = I_o e^{-\alpha c \ell}$$

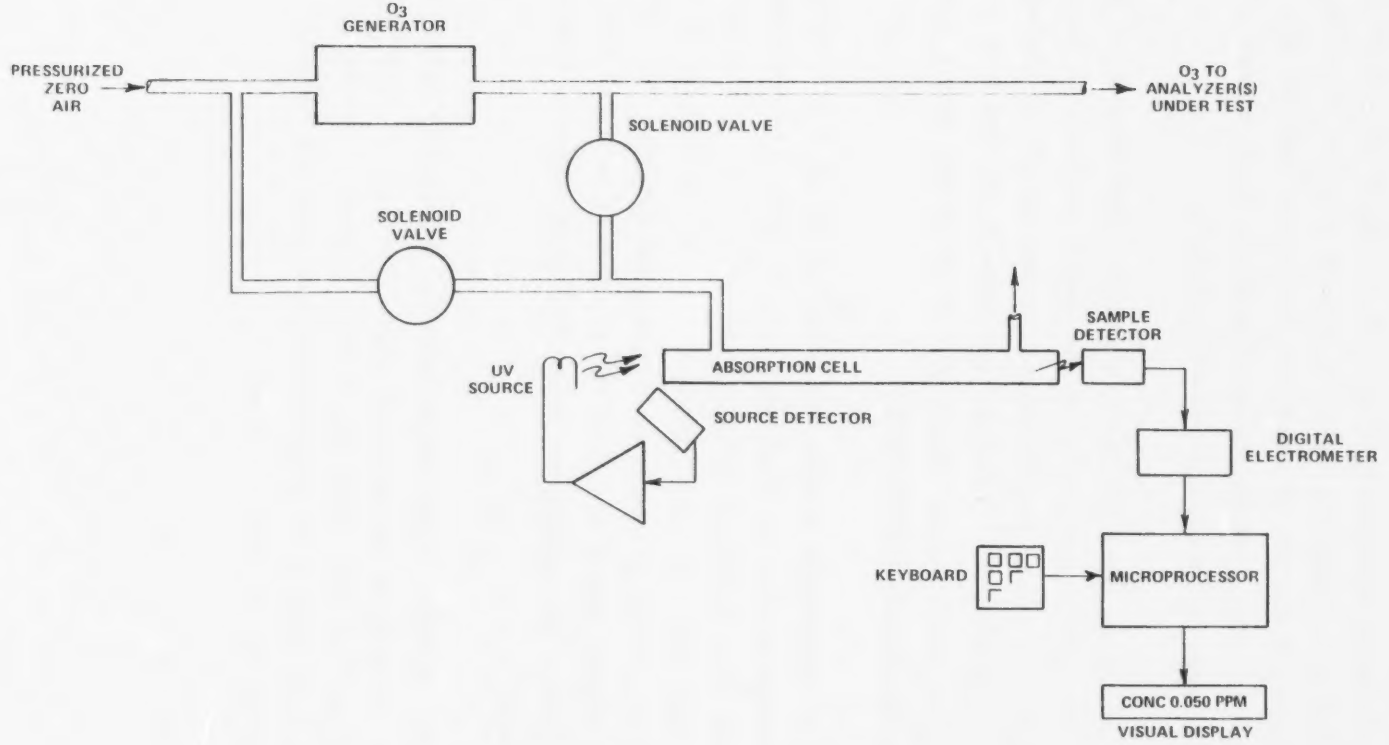


Figure 3-2. Simplified block diagram of Columbia Scientific Industries Corp. (CSI) Photocal 3000 Ozone Calibrator.

The concentration, c, is calculated as follows:

$$c = -\frac{10^6}{\alpha \ell} \ln \frac{I - I_d}{I_o - I_d}$$

where c = O_3 concentration in ppm
I = signal level with O_3 in the transmission path
I_o = signal level with no O_3 in the transmission path
I_d = system dark current
α = O_3 absorption coefficient
ℓ = transmission pathlength
10^6 = conversion factor from atmospheres to ppm

Continuous temperature and pressure measurements are made in the instrument and used to correct the calculation for the actual temperature and pressure of the sample.

When operating at zero O_3 concentration, the instrument may display a small "negative" concentration. This below-zero concentration is preceded by a minus sign and an error "E" is indicated in the display. This negative value should be added to the O_3 measurement as an offset, although it is generally too small to be of consequence.

The instrument has at least one source of error which may not be readily apparent to the operator: partial failure of a solenoid valve. The instrument measures the relative transmittance of a reference gas sample and an ozonized gas sample. If a solenoid valve should have a significant leak, the two gas samples are mixed to some degree and the difference in transmittance is reduced. This causes the instrument to indicate lower concentrations than are actually present. Leak-testing the valves is neither difficult nor time-consuming, and should be performed regularly.

REFERENCES

APHA Intersociety Committee. 1977. Methods of Air Sampling and Analysis (second ed.). American Public Health Association, Washington, D. C.

Becker, K. H., U. Schurath, and H. Seitz. 1974. Ozone Olefin Reactions in the Gas Phase. Rate Constants and Activation Energies. Int. J. Chem. Kinetics, 6:725.

Clyne, M. A. A., and J. A. Coxon. 1968. Kinetic Studies of Oxy-Halogen Radical Systems. Proc. Roy. Soc., A303:207.

DeMore, W. B., and O. Raper. 1964. Hartley Band Extinction Coefficients of Ozone in the Gas Phase and in Liquid Nitrogen, Carbon Monoxide, and Argon. J. Phys. Chem., 68:412.

Griggs, M. 1968. Absorption Coefficients of Ozone in the Ultraviolet and Visible Regions. J. Chem. Phys., 49:857.

Hampson, R. F. (ed.). 1973. Survey of Photochemical and Rate Data for Twenty-Eight Reactions of Interest in Atmospheric Chemistry. J. Phys. Chem. Ref. Data, 2:267.

Hearn, A. G. 1961. Absorption of Ozone in the Ultraviolet and Visible Regions of the Spectrum. Proc. Phys. Soc. (London), 78:932.

Inn, E. C. Y., and Y. Tanaka. 1953. Absorption Coefficient of Ozone in the Ultraviolet and Visible Regions. J. Opt. Soc. Am., 43:870.

McElroy, F. F. 1979. Transfer Standards for the Calibration of Ambient Air Monitoring Analyzers for Ozone. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

U.S. Environmental Protection Agency. 1979. Calibration of Ozone Reference Methods. Federal Register, 44:8221, February 8.

APPENDIX A

ULTRAVIOLET PHOTOMETRIC PROCEDURE FOR PRIMARY OZONE STANDARDS*

CALIBRATION PROCEDURE

1. Principle. The calibration procedure is based on the photometric assay of ozone (O_3) concentrations in a dynamic flow system. The concentration of O_3 in an absorption cell is determined from a measurement of the amount of 254 nm light absorbed by the sample. This determination requires knowledge of (1) the absorption coefficient (α) of O_3 at 254 nm, (2) the optical path length (ℓ) through the sample, (3) the transmittance of the sample at a wavelength of 254 nm, and (4) the temperature (T) and pressure (P) of the sample. The transmittance is defined as the ratio I/I_o, where I is the intensity of light which passes through the cell and is sensed by the detector when the cell contains an O_3 sample, and I_o is the intensity of light which passes through the cell and is sensed by the detector when the cell contains zero air. It is assumed that all conditions of the system, except for the contents of the absorption cell, are identical during measurement of I and I_o. The quantities defined above are related by the Beer-Lambert absorption law,

$$\text{Transmittance} = \frac{I}{I_o} = e^{-\alpha C \ell} \qquad (1)$$

where: α = absorption coefficient of O_3 at 254 nm = 308 ± 4 atm^{-1} cm^{-1} at 0°C and 760 torr. (1,2,3,4,5,6,7)

C = O_3 concentration in atmospheres

ℓ = optical path length in cm

*Extracted from the Code of Federal Regulations, Title 40, Part 50, Appendix D, as amended February 8, 1979 (Federal Register, 44:8221-8233).

APPENDIX A. ULTRAVIOLET PHOTOMETRIC PROCEDURE/Principle

In practice, a stable O_3 generator is used to produce O_3 concentrations over the required range. Each O_3 concentration is determined from the measurement of the transmittance (I/I_o) of the sample at 254 nm with a photometer of path length ℓ and calculated from the equation,

$$c(atm) = -\frac{1}{\alpha\ell} (\ln I/I_o) \qquad (2a)$$

or,

$$c(ppm) = -\frac{10^6}{\alpha\ell} (\ln I/I_o) \qquad (2b)$$

The calculated O_3 concentrations must be corrected for O_3 losses which may occur in the photometer and for the temperature and pressure of the sample.

2. Applicability. This procedure is applicable to the calibration of ambient air O_3 analyzers, either directly or by means of a transfer standard certified by this procedure. Transfer standards must meet the requirements and specifications set forth in Reference 8.

3. Apparatus. A complete UV calibration system consists of an ozone generator, an output port or manifold, a photometer, an appropriate source of zero air, and other components as necessary. The configuration must provide a stable ozone concentration at the system output and allow the photometer to accurately assay the output concentration to the precision specified for the photometer (3.1). Figure 1 shows a commonly used configuration and serves to illustrate the calibration procedure which follows. Other configurations may require appropriate variations in the procedural steps. All connections between components in the calibration system downstream of the O_3 generator should be of glass, Teflon, or other relatively inert material. Additional information regarding the assembly of a UV photometric calibration apparatus is given in Reference 9. For certification of transfer standards which provide their own source of O_3, the transfer standard may replace the O_3 generator and possibly other components shown in Figure 1; see Reference 8 for guidance.

APPENDIX A. ULTRAVIOLET PHOTOMETRIC PROCEDURE/Apparatus

3.1 UV photometer. The photometer consists of a low-pressure mercury discharge lamp, (optional) collimation optics, an absorption cell, a detector, and signal-processing electronics, as illustrated in Figure 1. It must be capable of measuring the transmittance, I/I_o, at a wavelength of 254 nm with sufficient precision such that the standard deviation of the concentration measurements does not exceed the greater of 0.005 ppm or 3% of the concentration. Because the low-pressure mercury lamp radiates at several wavelengths, the photometer must incorporate suitable means to assure that no O_3 is generated in the cell by the lamp, and that at least 99.5% of the radiation sensed by the detector is 254 nm radiation. (This can be readily achieved by prudent selection of optical filter and detector response characteristics.) The length of the light path through the absorption cell must be known with an accuracy of at least 99.5%. In addition, the cell and associated plumbing must be designed to minimize loss of O_3 from contact with cell walls and gas handling components. See Reference 9 for additional information.

3.2 Air flow controllers. Devices capable of regulating air flows as necessary to meet the output stability and photometer precision requirements.

3.3 Ozone generator. Device capable of generating stable levels of O_3 over the required concentration range.

3.4 Output manifold. The output manifold should be constructed of glass, Teflon, or other relatively inert material, and should be of sufficient diameter to insure a negligible pressure drop at the photometer connection and other output ports. The system must have a vent designed to insure atmospheric pressure in the manifold and to prevent ambient air from entering the manifold.

3.5 Two-way valve. Manual or automatic valve, or other means to switch the photometer flow between zero air and the O_3 concentration.

3.6 Temperature indicator. Accurate to ±1°C.

3.7 Barometer or pressure indicator. Accurate to ±2 torr.

4. Reagents.

4.1 Zero air. The zero air must be free of contaminants which would cause a detectable response from the O_3 analyzer, and it should be free of NO, C_2H_4, and other species which react with O_3. A procedure for generating suitable zero air is given in Reference 9. As shown in Figure 1, the zero air supplied to the photometer cell for the I_o reference measurement must be derived from the same source as the zero air used for generation of the ozone concentration to be assayed (I measurement). When using the photometer to certify a transfer standard having its own source of ozone, see Reference 8 for guidance on meeting this requirement.

5. Procedure.

5.1 General operation. The calibration photometer must be dedicated exclusively to use as a calibration standard. It should always be used with clean, filtered calibration gases, and never used for ambient air sampling. Consideration should be given to locating the calibration photometer in a clean laboratory where it can be stationary, protected from physical shock, operated by a responsible analyst, and used as a common standard for all field calibrations via transfer standards.

5.2 Preparation. Proper operation of the photometer is of critical importance to the accuracy of this procedure. The following steps will help to verify proper operation. The steps are not necessarily required prior to each use of the photometer. Upon initial operation of the photometer, these steps should be carried out frequently, with all quantitative results or indications recorded in a chronoloigcal record either in tabular form or plotted on a graphical chart. As the performance and stability record of the photometer

is established, the frequency of these steps may be reduced consistent with the documented stability of the photometer.

5.2.1 Instruction manual: Carry out all set-up and adjustment procedures or checks as described in the operation or instruction manual associated with the photometer.

5.2.2 System check: Check the photometer system for integrity, leaks, cleanliness, proper flowrates, etc. Service or replace filters and zero air scrubbers or other consumable materials, as necessary.

5.2.3 Linearity: Verify that the photometer manufacturer has adequately established that the linearity error of the photometer is less than 3%, or test the linearity by dilution as follows: Generate and assay an O_3 concentration near the upper range limit of the system (0.5 or 1.0 ppm), then accurately dilute that concentration with zero air and reassay it. Repeat at several different dilution ratios. Compare the assay of the original concentration with the assay of the diluted concentration divided by the dilution ratio, as follows:

$$E = \frac{A_1 - A_2/R}{A_1} \times 100\% \qquad (3)$$

where: E = linearity error, percent

A_1 = assay of the original concentration

A_2 = assay of the diluted concentration

R = dilution ratio = flow of original concentration divided by the total flow

The linearity error must be less than 5%. Since the accuracy of the measured flowrates will affect the linearity error as measured this way, the test is not necessarily conclusive. Additional information on verifying linearity is contained in Reference 9.

5.2.4 Intercomparison: When possible, the photometer should be occasionally intercompared, either directly or via transfer standards, with calibration photometers used by other agencies or laboratories.

5.2.5 Ozone losses: Some portion of the O_3 may be lost upon contact with the photometer cell walls and gas handling components. The magnitude of this loss must be determined and used to correct the calculated O_3 concentration. This loss must not exceed 5%. Some guidelines for quantitatively determining this loss are discussed in Reference 9.

5.3 Assay of O_3 concentrations.

5.3.1 Allow the photometer system to warm up and stabilize.

5.3.2 Verify that the flowrate through the photometer absorption cell, F_p, allows the cell to be flushed in a reasonably short period of time (2 liter/min is a typical flow). The precision of the measurements is inversely related to the time required for flushing, since the photometer drift error increases with time.

5.3.3 Insure that the flowrate into the output manifold is at least 1 liter/min greater than the total flowrate required by the photometer and any other flow demand connected to the manifold.

5.3.4 Insure that the flowrate of zero air, F_z, is at least 1 liter/min greater than the flowrate required by the photometer.

5.3.5 With zero air flowing in the output manifold, actuate the two-way valve to allow the photometer to sample first the manifold zero air, then F_z. The two photometer readings must be equal ($I = I_o$).

NOTE: In some commercially available photometers, the operation of the two-way valve and various other operations in section 5.3 may be carried out automatically by the photometer.

5.3.6 Adjust the O_3 generator to produce an O_3 concentration as needed.

5.3.7 Actuate the two-way valve to allow the photometer to sample zero air until the absorption cell is thoroughly flushed and record the stable measured value of I_o.

5.3.8 Actuate the two-way valve to allow the photometer to sample the ozone concentration until the absorption cell is thoroughly flushed and record the stable measured value of I.

5.3.9 Record the temperature and pressure of the sample in the photometer absorption cell. (See Reference 9 for guidance.)

5.3.10 Calculate the O_3 concentration from equation 4. An average of several determinations will provide better precision.

$$[O_3]_{OUT} = \left(\frac{-1}{\alpha \ell} \ln \frac{I}{I_o}\right) \left(\frac{T}{273}\right) \left(\frac{760}{P}\right) \left(\frac{10^6}{L}\right) \qquad (4)$$

where: $[O_3]_{OUT}$ = O_3 concentration, ppm

α = absorption coefficient of O_3 at 254 nm = 308 atm^{-1} cm^{-1} at 0°C and 760 torr

ℓ = optical path length, cm

T = sample temperature, K

P = sample pressure, torr

L = correction factor for O_3 losses from 5.2.5 = (1-fraction O_3 lost).

NOTE: Some commercial photometers may automatically evaluate all or part of equation 4. It is the operator's responsibility to verify that all of the information required for equation 4 is obtained, either automatically by the photometer or manually. For "automatic" photometers which evaluate the first

term of equation 4 based on a linear approximation, a manual correction may be required, particularly at higher O_3 levels. See the photometer instruction manual and Reference 9 for guidance.

5.3.11 Obtain additional O_3 concentration standards as necessary by repeating steps 5.3.6 to 5.3.10 or by Option 1.

5.4 Certification of transfer standards. A transfer standard is certified by relating the output of the transfer standard to one or more ozone standards as determined according to section 5.3. The exact procedure varies depending on the nature and design of the transfer standard. Consult Reference 8 for guidance.

5.5 Calibration of ozone analyzers. Ozone analyzers are calibrated as follows, using ozone standards obtained directly according to section 5.3 or by means of a certified transfer standard.

5.5.1 Allow sufficient time for the O_3 analyzer and the photometer or transfer standard to warm up and stabilize.

5.5.2 Allow the O_3 analyzer to sample zero air until a stable response is obtained and adjust the O_3 analyzer's zero control. Offsetting the analyzer's zero adjustment to + 5% of scale is recommended to facilitate observing negative zero drift. Record the stable zero air response as "Z".

5.5.3 Generate an O_3 concentration standard of approximately 80% of the desired upper range limit (URL) of the O_3 analyzer. Allow the O_3 analyzer to sample this O_3 concentration standard until a stable response is obtained.

5.5.4 Adjust the O_3 analyzer's span control to obtain a convenient recorder response as indicated below:

$$\text{recorder response (\% scale)} = \left(\frac{[O_3]_{OUT}}{URL} \times 100\right) + Z \qquad (5)$$

where: URL = upper range limit of the O_3 analyzer, ppm
Z = recorder response with zero air, % scale

Record the O_3 concentration and the corresponding analyzer response. If substantial adjustment of the span control is necessary, recheck the zero and span adjustments by repeating steps 5.5.2 to 5.5.4.

5.5.5 Generate several other O_3 concentration standards (at least 5 others are recommended) over the scale range of the O_3 analyzer by adjusting the O_3 source or by Option 1. For each O_3 concentration standard, record the O_3 concentration and the corresponding analyzer response.

5.5.6 Plot the O_3 analyzer responses versus the corresponding O_3 concentrations and draw the O_3 analyzer's calibration curve or calculate the appropriate response factor.

5.5.7 Option 1: The various O_3 concentrations required in steps 5.3.11 and 5.5.5 may be obtained by dilution of the O_3 concentration generated in steps 5.3.6 and 5.5.3. With this option, accurate flow measurements are required. The dynamic calibration system may be modified as shown in Figure 2 to allow for dilution air to be metered in downstream of the O_3 generator. A mixing chamber between the O_3 generator and the output manifold is also required. The flowrate through the O_3 generator (F_O) and the dilution air flowrate (F_D) are measured with a reliable flow or volume standard traceable to NBS. Each O_3 concentration generated by dilution is calculated from:

$$[O_3]'_{OUT} = [O_3]_{OUT} \left(\frac{F_O}{F_O + F_D}\right) \qquad (6)$$

where: $[O_3]'_{OUT}$ = diluted O_3 concentration, ppm

F_O = flowrate through the O_3 generator, liter/min

F_D = diluent air flowrate, liter/min

REFERENCES

1. E.C.Y. Inn and Y. Tanaka, "Absorption Coefficient of Ozone in the Ultraviolet and Visible Regions". *J. Opt. Soc. Am.*, 43,870 (1953).

2. A.G. Hearn, "Absorption of Ozone in the Ultraviolet and Visible Regions of the Spectrum", *Proc. Phys. Soc.* (London), 78,932 (1961).

3. W.B. DeMore and O. Raper, "Hartley Band Extinction Coefficients of Ozone in the Gas Phase and in Liquid Nitrogen, Carbon Monoxide, and Argon", *J. Phys. Chem.*, 68,412 (1964).

4. M. Griggs, "Absorption Coefficients of Ozone in the Ultraviolet and Visible Regions", *J. Chem. Phys.*, 49,857 (1968).

5. K.H. Becker, U. Schurath, and H. Seitz, "Ozone Olefin Reactions in the Gas Phase. 1. Rate Constants and Activation Energies", *Int'l. J. Chem. Kinetics*, VI,725 (1974).

6. M.A.A. Clyne and J.A. Coxom. "Kinetic Studies of Oxy-Halogen Radical Systems", *Proc. Roy. Soc.*, A303,207 (1968).

7. J.W. Simons, R.J. Paur, H.A. Webster, and E.J. Bair, "Ozone Ultraviolet Photolysis. VI. The Ultraviolet Spectrum", *J. Chem. Phys.*, 59, 1203 (1973).

8. "Transfer Standards for Calibration of Ambient Air Monitoring Analyzers for Ozone", EPA publication available from EPA, Department E (MD-77), Research Triangle Park, North Carolina 27711.

9. "Technical Assistance Document for the Calibration of Ambient Ozone Monitors", EPA publication available from EPA, Department E (MD-77), Research Triangle Park, North Carolina 27711.

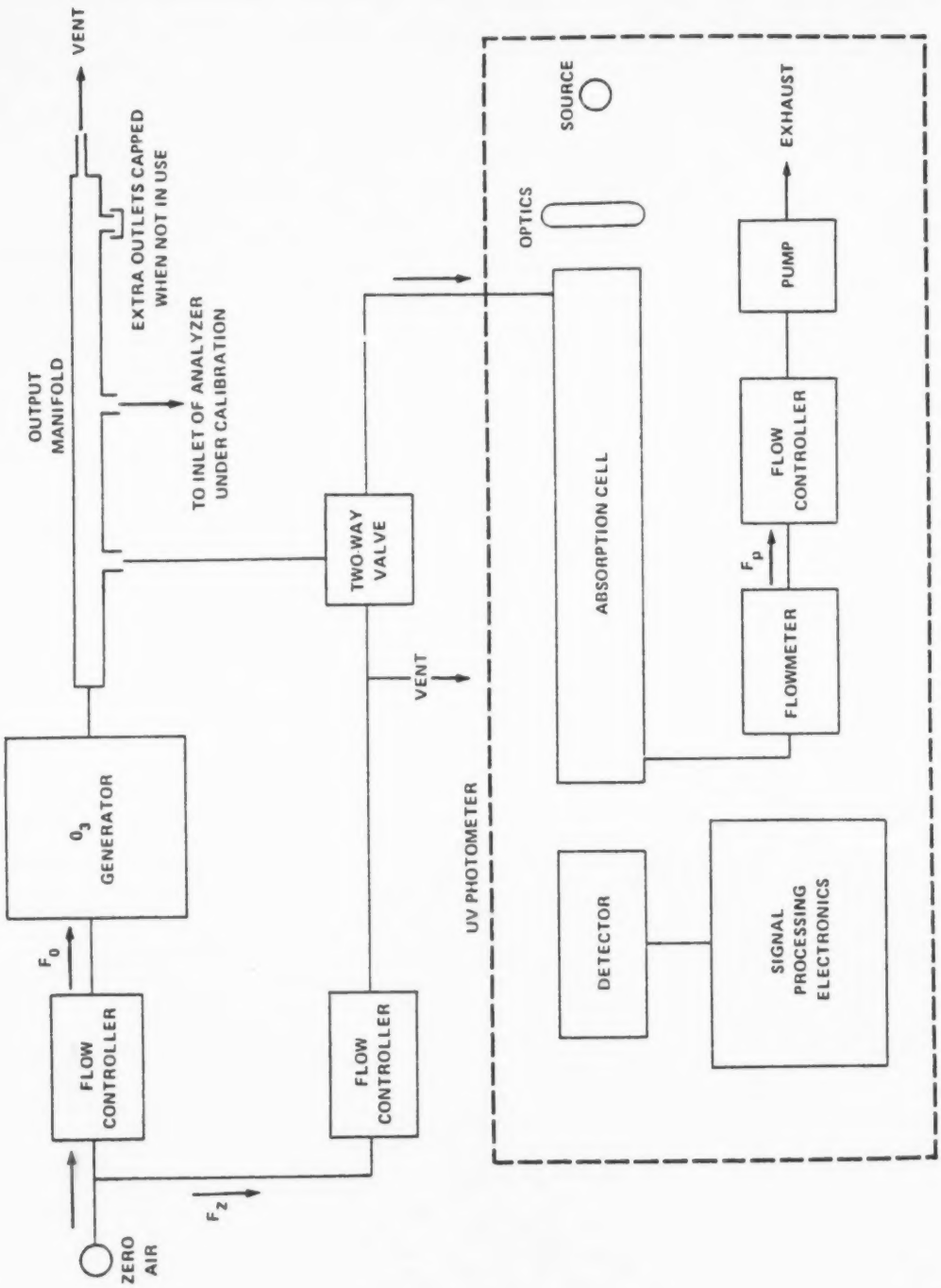


Figure 1. Schematic diagram of a typical UV photometric calibration system.

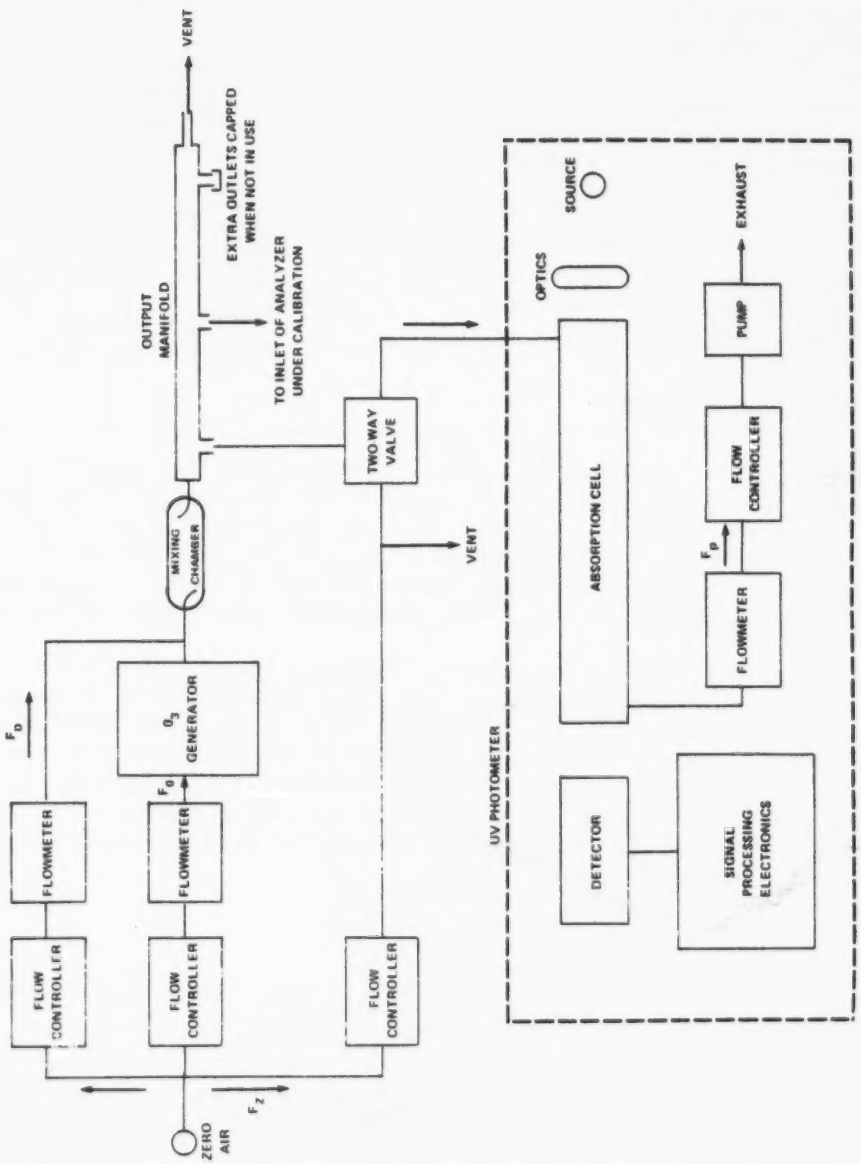


Figure 2. Schematic diagram of a typical UV photometric calibration system (Option 1).